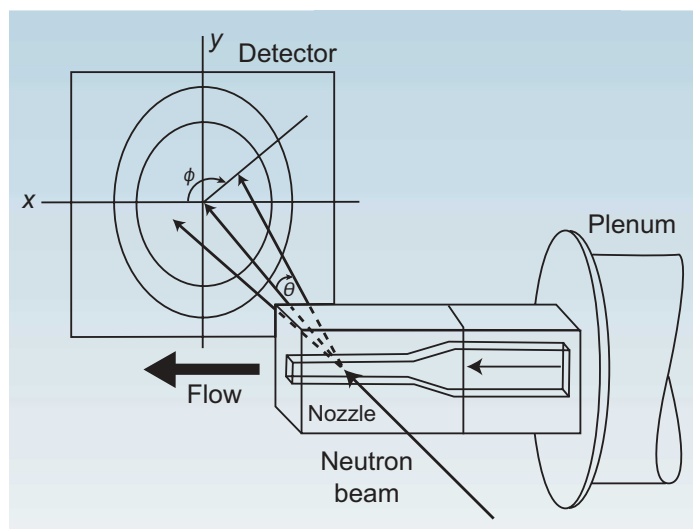


# Probing the Structure of Aerosol Nanodroplets

**N**anodroplet aerosols form readily in the supersonic expansions that occur, for example, in turbomachinery, jet exhausts, and volcanic eruptions. Thus, understanding particle formation and growth when cooling rates approach  $10^6$  K/s is of broad scientific interest.

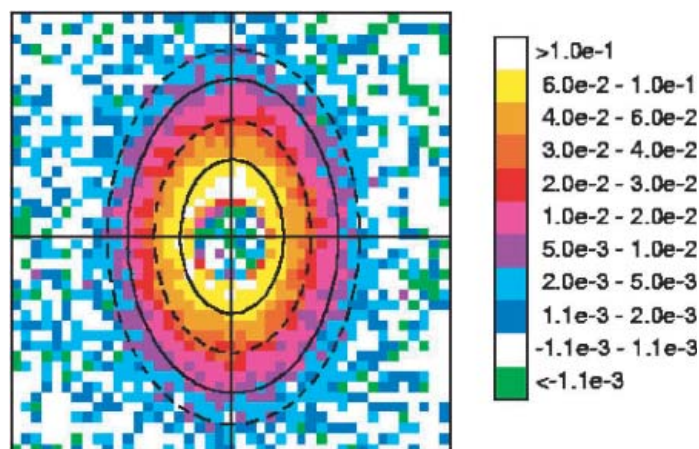
From a fundamental point of view, particles with radii  $< 10$  nm are important because they lie in the critical transition zone between large molecular clusters and bulk material. In multicomponent droplets, there is also strong theoretical evidence for surface enrichment, i.e., that the surface and interior compositions can differ significantly. Surface enrichment is important because it affects nucleation, growth and evaporation kinetics, and the heterogeneous chemistry of aerosol droplets. A major goal of our work is to use small angle neutron scattering to find direct evidence for surface enrichment in nanodroplets.

We produce nanodroplets with radii between 5 nm and 12 nm and number densities in the range of  $10^{11}$   $\text{cm}^{-3}$  to  $10^{12}$   $\text{cm}^{-3}$  by rapidly expanding a dilute vapor mixture of  $\text{D}_2\text{O}$  (or other condensable) and  $\text{N}_2$  in a supersonic nozzle apparatus (Fig. 1) [1]. The volume fraction of droplets is always



**FIGURE 1.** The nozzle is placed in the sample chamber at right angles to the neutron beam.

less than  $10^{-5}$  and, thus, the scattering signals are close to the instrument background. Furthermore, the high velocity of the droplets (400 m/s to 500 m/s) is comparable to the speed of the neutrons. This leads to a Doppler shift in the momentum of the scattered neutrons [2, 3], and the 2-D scattering



**FIGURE 2.** The observed 2-D scattering pattern for an aerosol with an average particle velocity  $v_p = 435$  m/s measured using a neutron wavelength of  $\lambda = 1.0$  nm ( $v_n = 400$  m/s). The contour levels correspond to absolute intensities of 0.08, 0.03, 0.008 and 0.003  $\text{cm}^{-1}$ , respectively.

patterns are anisotropic (Fig. 2) even though spherical droplets at rest scatter isotropically. This Doppler shift can be used to directly measure the velocity of the particles, and, in a test case, this velocity was within 2 % of the average velocity derived from the pressure trace measurements [2].

Rather than simply examine nanodroplets for which segregation of the components is severe, we use different materials to observe the transition between well-mixed and fully segregated droplets. Thus, our experiments include binary mixtures of  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , ethanol, and n-butanol, or its fully deuterated analog d-butanol. Almost degenerate mixtures, such as  $\text{D}_2\text{O} - \text{H}_2\text{O}$ , appear to form well-mixed droplets [4]. In contrast, binary nanodroplets containing  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ) and a low molar concentration of d-butanol (or h-butanol) should consist of a water-rich core and an

alcohol-rich shell. Our recent SANS experiments with  $\text{H}_2\text{O}$  – d-butanol nanodroplets clearly demonstrate for the first time the existence of the alcohol-rich shell. As illustrated in Fig. 3, for these droplets the scattered intensity falls off as  $q^{-2}$  in the high  $q$  region, as is characteristic for scattering by a shell. Furthermore, the feature in the region  $0.4 \text{ nm}^{-1} < q < 0.5 \text{ nm}^{-1}$  cannot be reproduced by a well-mixed droplet model that matches the low  $q$  data. Also shown in Fig. 3 is the scattering spectrum from the complementary  $\text{D}_2\text{O}$  – h-butanol experiment. As expected, the scattered intensity is much higher, and the signal intensity decreases as  $q^{-4}$  in the high  $q$  region. In this case, the  $\text{D}_2\text{O}$ -rich core dominates the scattering.

In summary, SANS provides us with a powerful new way to study the properties of nanometer sized liquid droplets in the environment in which they form. To date, it is the only technique to directly probe the microstructure of aerosol nanodroplets. Combined with pressure trace measurements and modeling, SANS provides information critical to our understanding of droplet formation and growth in the nanometer size regime.

## References

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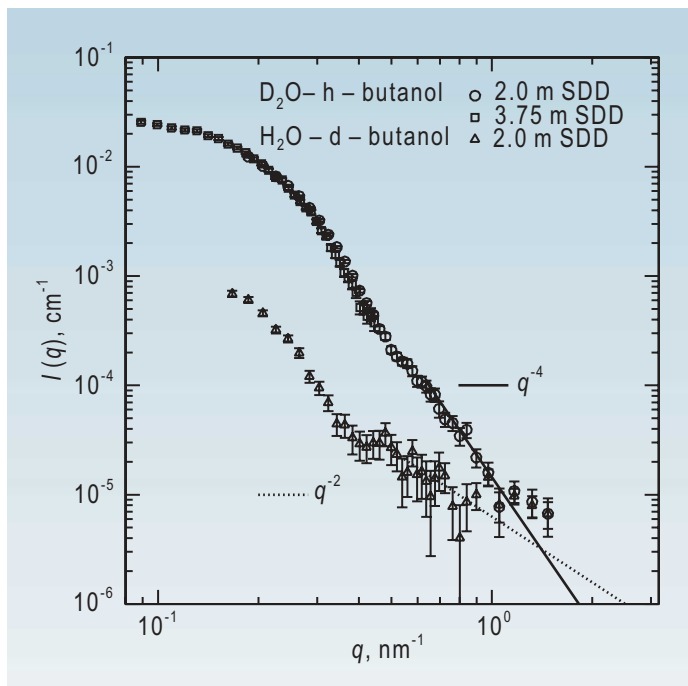


FIGURE 3. Scattering from a  $\text{D}_2\text{O}$  – h-butanol aerosol is compared to that from a  $\text{H}_2\text{O}$  – d-butanol aerosol formed under identical conditions in the nozzle. Both aerosols contain  $\approx 6\%$  molecular fraction butanol. In the high  $q$  region, the intensity falls off as  $q^{-4}$  for the  $\text{D}_2\text{O}$ -rich droplets, but only as  $q^{-2}$  for the  $\text{H}_2\text{O}$ -rich droplets. Our preliminary modeling shows that the feature in the region  $0.4 \text{ nm}^{-1} < q < 0.5 \text{ nm}^{-1}$  of the  $\text{H}_2\text{O}$  – d-butanol spectrum cannot be reproduced by a well mixed droplet model. SDD is the sample-to-detector distance.